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Tracking the onset of Phanerozoic-style redox-sensitive trace metal enrichments: New results from basal Ediacaran post-glacial strata in NW Canada

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ABSTRACT

A global rise in oxygen levels has been proposed to coincide with the Ediacaran to Cambrian radiation of animals, yet the precise timing and nature of this change remains unresolved. One hypothesis is that the ocean/atmosphere system became temporarily well-oxygenated in the earliest Ediacaran, directly following the Marinoan Snowball Earth glaciation (~635 Ma). The evidence for oxygenation is based on large enrichments of redox-sensitive trace elements in black shale from South China presumably deposited under a euxinic water column. These enrichments meet or exceed the bulk concentrations of redox-sensitive trace elements found in Phanerozoic shale deposited under euxinic water columns. Here we test the early Ediacaran post-Snowball oxygenation hypothesis with new data from a high-resolution, multi-proxy geochemical and sedimentological study of three stratigraphic sections in the earliest Ediacaran Sheepbed Formation of the Mackenzie and Wernecke Mountains, NW Canada. Iron speciation data from all sections suggest that the local water column was dominantly ferruginous, with a notable exception of probable euxinic conditions recorded in part of one section. Redox-sensitive elements show no appreciable enrichments in the basal Sheepbed Formation, with maximum concentrations of molybdenum, vanadium, uranium and chromium only slightly above world average shale values. The lack of substantial elemental enrichments within the Sheepbed Formation is consistent with results from coeval ferruginous strata in Svalbard. The dominance of local ferruginous conditions in NW Canada cannot alone account for the muted redox-sensitive element enrichments as V, U, and Cr are thought to be enriched under these conditions, and samples deposited under euxinic conditions also lack Phanerozoic-style enrichments. These contrasting results from different localities highlight a need to further investigate the veracity of trace metal enrichments in all localities as representing global redox conditions as the results have important implications for the timing of oxygenation with respect to early animal evolution.

1. Introduction

The Ediacaran Period (ca. 635 Ma–541 Ma) witnessed a variety of profound environmental changes, including the termination of low-latitude Snowball Earth glaciations, large perturbations to the geochemical cycles of carbon and sulfur, and dynamic redox shifts in the Earth's ocean/atmosphere system (Fike et al., 2006; Halverson et al., 2010; Lyons et al., 2014). During this pivotal time in Earth's history, there was a radical shift in the fossil record from mostly microscopic prokaryotic assemblages to large, complex macrofossils in the mid- to late-Ediacaran and finally to the shelly animal fauna of the Cambrian (Xiao and Laflamme, 2009; Erwin et al., 2011). Although the relationship is not established with certainty, a rise in oxygen is commonly believed to have played a fundamental role in biological evolution through the Ediacaran-Cambrian transition, acting either directly in factors such as body size, or indirectly in allowing for the evolution of predators and a resulting predator-prey 'arms race' (Sperling et al., 2013a).

Geochemical redox proxies from global sedimentary successions have been used to reconstruct an array of temporal hypotheses for the timing of ocean/atmosphere oxygenation during the terminal Neoproterozoic. Initial studies, focused on iron speciation and sulfur isotopes ($\delta^{34}S$), proposed widespread oxygenation following the ca. 580 Ma Gaskiers glaciation (Canfield et al., 2007; Fike et al., 2006). In

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contrast, more recent work focused on redox-sensitive element (RSE) enrichments from South China has promoted a more nuanced oxygenation history, where oxygen levels rose substantially in the earliest Ediacaran following the ca. 635 Ma Marinoan glaciation (Sahoo et al., 2012). This evidence lends support to the hypothesis that a post-glacial nutrient surplus fueled ocean oxygenation (Elie et al., 2007; Kirschvink et al., 2000; Kunzmann et al., 2013, 2015; Planavsky et al., 2010). The evidence for high oxygen levels (based on RSE enrichments; discussed below) abruptly disappears in the early Ediacaran (Sahoo et al., 2012), leading to the suggestion that this transitory first spike in oxygen levels was one of several transitory Ocean Oxygenation Events (OOEs) punctuating a generally reducing Ediacaran ocean (Sahoo et al., 2016).

Redox-sensitive elements have great utility in addressing the global areal extent of oxic conditions at the sediment-water interface. Many of these elements have relatively low crustal abundances and low riverine fluxes from oxidative weathering in surface environments (Emerson and Huested, 1991; Turekian and Wedepohl, 1961). These attributes, combined with their long residence times in seawater, allow them to be used to track the global ocean redox state (Emerson and Huested, 1991). For elements such as uranium, molybdenum, vanadium and chromium, deposition in sediment under reducing water columns is their most effective sink (Emerson and Huested, 1991; Tribovillard et al., 2006). Therefore, the major control on the RSE concentrations in seawater is the geographic extent of these reducing sinks, specifically the global proportion of reducing versus oxic conditions at the sediment-water interface (Algeo, 2004; Emerson and Huested, 1991; Gill et al., 2011; Morford and Emerson, 1999; Owens et al., 2016; Partin et al., 2013b; Pearce et al., 2008; Reinhard et al., 2013; Sahoo et al., 2012; Sahoo et al., 2016; Scott et al., 2008). If the area of reducing environments is expanded beyond a critical threshold, the sinks outpace the source flux, resulting in a net decrease of RSE concentrations in seawater (Fig. 1; Sahoo et al., 2012; Scott et al., 2008). Because authigenic sediment enrichment is positively correlated to seawater RSE concentrations (e.g., Algeo and Lyons, 2006; Scott et al., 2013a), sediment deposited under anoxic water columns during times of globally expansive reducing conditions will display comparatively low RSE enrichments. The opposite is also true—as oceans become well-oxygenated, seawater RSE concentrations should increase globally, resulting in a distinct fingerprint of high RSE enrichments in local anoxic sedimentary basins, akin to those recorded in Phanerozoic anoxic shale (i.e., 'Phanerozoic-style' enrichments; Fig. 1; Sahoo et al., 2012; Scott et al., 2008). Thus, RSE enrichments in strata known to be deposited under anoxic conditions can be informative about the global redox landscape.

In South China, an early Ediacaran pulse of RSE enrichments in Mo (to 172 mg/kg), V (to 6417 mg/kg), and U (to 33 mg/kg) was observed in black shale of Member II of the Doushantuo Formation, directly above Marinoan glacial deposits and the associated cap carbonate, and interpreted to represent ephemeral global ocean oxygenation (Sahoo et al., 2012). Multiple RSE concentration spikes up-section in the Doushantuo Formation at the Wuhe locality were used as evidence to suggest this post-Marinoan event was the first of several OOEs (Sahoo et al., 2016). Depleted pyrite sulfur isotope ratios from these same stratigraphic intervals were interpreted as the result of an expanded seawater sulfate reservoir, consistent with global oxygenation (Sahoo et al., 2012, 2016). These OOEs have been labeled sequentially through time, with the first post-Marinoan enrichment termed OOE-A. If the global ocean was well oxygenated during these OOEs, other localities worldwide should either: 1) exhibit an oxic signature, or 2) be interpreted as anoxic and record similar patterns of 'Phanerozoic-style' enrichments in RSEs. Neither appears to be the case for data published to date from other coeval localities. For example, iron speciation data from Svalbard highlights a persistently ferruginous to sub-oxic shelf environment throughout the Neoproterozoic with muted Mo, V, and U concentrations (Kunzmann et al., 2015). Iron speciation data from the Wernecke Mountains of Yukon also show a dominantly ferruginous shelf environment at the beginning of the Ediacaran with muted Mo and V enrichments (Johnston et al., 2013). However, direct comparison of the RSE records in these studies with the basal Ediacaran record of South China is challenging due to differences in sampling density, poor temporal constraints on sampled sections, predominance of ferruginous conditions preserved in other Ediacaran successions (rather than euxinic conditions as in modern analogues), and the extremely condensed nature of the South China sections compared to normal marine shale successions.

The Ediacaran stratigraphic record in NW Canada provides an excellent location to test the transitory OOE framework proposed by Sahoo et al. (2012, 2016). Here, we present new multi-proxy geochemical data

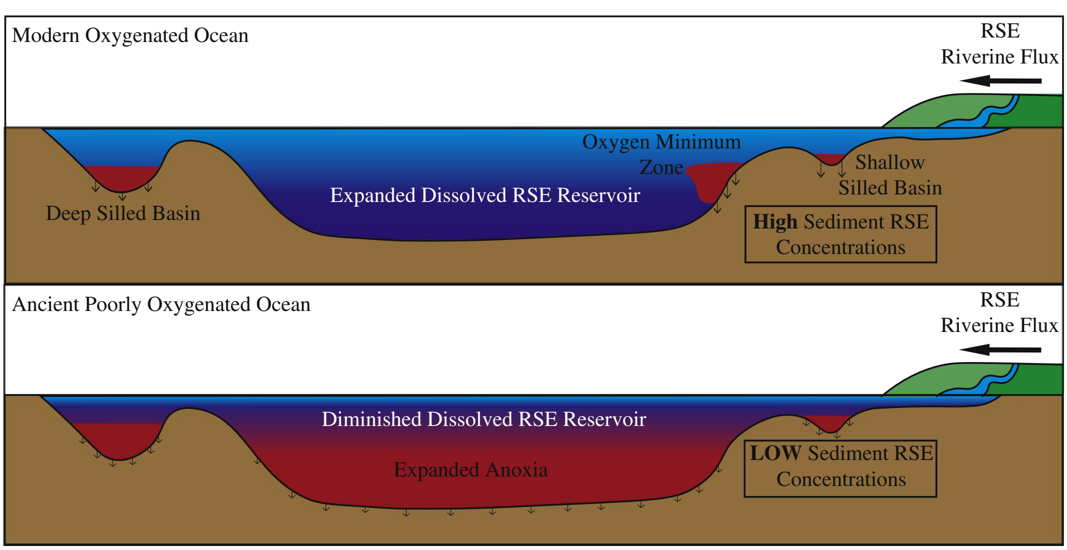

Fig. 1. A comparison of modern oxygenated and ancient poorly oxygenated ocean RSE cycling. The main RSE sinks are sediments deposited under reducing conditions. As anoxic conditions are rare in the modern ocean, the oceanic RSE inventory is high. Because authigenic RSE enrichment is a function of dissolved RSE levels, anoxic shale deposited in the modern (and much of the Phanerozoic) exhibit large RSE enrichments. Conversely, in ancient poorly oxygenated oceans, the areal extent of anoxic conditions can crash the dissolved RSE reservoirs in seawater. As a result, sediment deposited underneath an anoxic water column would exhibit muted enrichments. See Algeo (2004), Scott et al. (2008), Sahoo et al. (2012), and text for further discussion.